

IMPROVEMENT OF HIGH TEMPERATURE STRENGTH OF TYPE 304
STAINLESS STEEL BY SMALL ADDITIONS OF TITANIUM
AND NIOBIUM

T. Shinoda, T. Mimino, K. Kanoshita
and I. Minegishi

Translation of "Biryō no Ti to Nb Tenka
ni yoru 304-kei sutenresu-kō no kōon
kyōdo no kaizen", Tetsu-To-Hagane Over-
seas (Nihon Tekko Kyokai. Transactions
of the Iron and Steel Institute of
Japan), December, 1968, Vol. 54, No. 14,
pp. 1472 - 1486

(NASA-TT-F-16044) IMPROVEMENT OF HIGH
TEMPERATURE STRENGTH OF TYPE 304
STAINLESS STEEL BY SMALL ADDITIONS OF
TITANIUM AND (Scientific Translation
Service) 38 p HC \$3.75

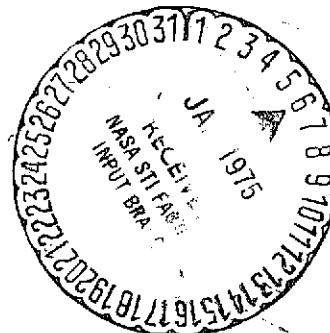
CSCL 11F

G3/26

N75-13087

Unclas.

04951



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C. 20546 DECEMBER 1974

1. Report No. NASA 16,044	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle IMPROVEMENT OF HIGH TEMPERATURE STRENGTH OF TYPE 304 STAINLESS STEEL BY SMALL ADDITIONS OF TITANIUM AND NIOBIUM		5. Report Date December 1974	
		6. Performing Organization Code	
7. Author(s) T. Shinoda, T. Mimino, K. Kinoshita and I. Minegishi		8. Performing Organization Report No.	
		10. Work Unit No.	
9. Performing Organization Name and Address SCITRAN Box 5456 Santa Barbara, CA 93108		11. Contract or Grant No. NASW-2483	
		13. Type of Report and Period Covered Translation	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		14. Sponsoring Agency Code	
15. Supplementary Notes Translation of "Biryō no Ti to Nb Tenka ni yoru 304-kei sutenresu-kō no kōon kyōdo no kaizen", Tetsu-To-Hagane Overseas (Nihon Tekko Kyokai. Transactions of the Iron and Steel Institute of Japan), December, 1968, Vol. 54, No. 14, pp. 1472 - 1486.			
16. Abstract A study was made of improving the high temperature strength of Type 304 stainless steel by additions of titanium and niobium. It was found that in 304 type steel, these additions made a marked improvement in the high temperature strength. It was also found that the creep rupture strength was higher.			
17. Key Words (Selected by Author(s))		18. Distribution Statement Unclassified - Unlimited	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 36	22. Price

IMPROVEMENT OF HIGH TEMPERATURE STRENGTH OF TYPE 304
STAINLESS STEEL BY SMALL ADDITIONS OF TITANIUM
AND NIOBIUM*

Takayuki Shinoda**, Tohru Mimino***,
Kazuhisa Kinoshita*** and Isao Minegishi***

ABSTRACT. Type 304H steel which shows the highest creep rupture strength in the tests of our laboratory has very high creep-rupture strength over long periods of time, and seems to have even higher strength than that of type 316H steel. If 403H steel were always available, the profit would be expected to reduce the construction cost of boiler plants.

The difference in the strength can be explained by the electron microscopic structure. The one with the higher strength has a very fine and good distribution of $M_{23}C_6$ type carbides, and they have a resistance to coalesce for longer times due to the presence of small amounts of titanium and niobium. An experimental type 304 steel containing 0.16% C, 0.10% Ti, and 0.15% Nb had much higher creep-rupture strength than type 316H steel, and proved to be a very economical new stainless steel for high temperature use. Also it was found that at

*Made public October, 1967, and April, 1968, at the Lecture-Meetings of this society. Received June 13, 1968.

**Tokyo Metal-Working University, Metals-Engineering Department. Formerly at Technical Laboratory of Japan Steel-Piping (Co.).

***Technical Laboratory, Japan Steel-Piping (Co.).

C/(Ti + Nb) atomic ratio of about 4, the maximum high temperature strength is obtained and precipitated carbides distribute themselves very finely and uniformly.

1. Introduction

With the appearance of supercritical-pressure boilers, steam has /1472* been subjected to increasingly high temperatures and pressures. The same is true of the materials used in them, and high-strength steel is in great demand. At present, the 18 - 8 line of stainless steel is being used, particularly in the piping of super-heaters and in main steam-pipes; but 321 steel, especially, is being used rather frequently. However, in 1965, the approved stress of the ASME boiler code was revised, and Type 304 H steel was to be used for 650° and above, thus establishing an approved stress higher than 321 and 347. Because of this, it is presumed that this steel type will be used widely.

Now, if we investigate the data [1] published by ASTM, and look at the creep-rupture strength of 304H steel compared with the other 18 - 8 line of stainless (316H, 321, and 347) steels, the scatter is very much larger. Naturally, high-strength creep steel, at temperatures of 650° C and above, shows a higher value than that of 316H steel. One of the authors also has reported [2] regarding the creep-rupture strength of the 18 - 8 line of stainless steel as steel-piping material for boiler use. In particular, the creep-rupture strength of 304H steel varied greatly, depending on the charge, and an extremely high rupture strength of 304H steel was obtainable. Even when the charge produced a low strength, the ASME authorized stress was fully satisfied.

The authors sought to find the reasons for such differences in creep rupture strength in 304H steel, as determined by the charge, and reached the conclusion that the differences in the precipitation

* Numbers in the margin indicate pagination in the original foreign text.

forms of the carbides and in their distribution patterns had an intimate connection with these differences in strength. Moreover, they discovered that, with the simultaneous addition of minute amounts of Ti and Nb, the precipitated carbides became finer. If one makes use of this phenomenon, it is possible to improve the high-temperature strength of Type 304 steel easily and remarkably. Therefore, we shall report on these results.

2. Tested Materials and Experimental Method

Table 1 shows the chemical composition of the steels used in the experiment. The A-order of the table was used to find the differences in strength, as governed by the charge; the B-order — to investigate the changes in strength brought about by the addition of small amounts of each kind of alloying element. The C-order includes the different steels where small amounts of Ti and Nb were added simultaneously.

TABLE 1. CHEMICAL COMPOSITION OF TYPE 304 AUSTENITIC STEELS USED (wt. %)

Series	Steel	C	Si	Mn	Cr	Ni	Mo	N	Ti	Nb	C/(Ti+Nb) atomic ratio
A	Ch.A	0.05	0.55	1.38	18.12	10.03	tr.	0.0273	0.014	tr.	—
	Ch.B	0.07	0.48	1.44	18.25	9.45	0.32	0.0472	0.014	0.003	—
B	C02	0.02	0.57	1.33	18.73	11.04	—	0.0329	—	—	—
	C12	0.12	0.58	1.33	18.56	11.09	—	0.0324	—	—	—
	C17	0.17	0.55	1.22	17.85	10.04	—	0.0328	—	—	—
	C23	0.23	0.55	1.32	18.56	11.09	—	0.0356	—	—	—
	Mo2	0.08	0.45	1.56	18.98	10.51	0.24	—	—	—	—
	Mo5	0.08	0.44	1.51	18.81	10.74	0.53	—	—	—	—
	N016	0.12	0.51	1.45	16.50	9.80	—	0.0164	tr.	tr.	—
	N115	0.12	0.60	1.40	18.11	9.62	—	0.1154	tr.	tr.	—
	T02	0.12	0.74	1.28	20.55	9.16	—	—	0.02	tr.	—
	NB34	0.14	0.58	1.50	15.59	11.56	—	—	tr.	0.34	—
C	TN1	0.03	0.70	1.51	17.83	9.57	tr.	—	0.10	0.18	0.62
	TN2	0.14	0.68	1.45	17.65	9.58	tr.	—	0.12	0.34	1.89
	TN3	0.13	0.58	1.47	18.47	9.86	0.43	—	0.09	0.29	2.15
	TN4	0.16	0.50	1.45	18.20	9.86	tr.	—	0.08	0.30	2.72
	TN5	0.16	0.58	1.47	18.29	9.16	tr.	—	0.09	0.13	4.06
	TN6	0.12	0.68	1.20	20.28	9.57	tr.	—	0.02	0.10	6.80
	TN7	0.12	0.72	1.14	20.37	9.27	tr.	—	0.03	0.02	11.90

P=0.07~0.018, S=0.009~0.024, Cu=0.02~0.04

The A-order was case in a 15 ton electric arc furnace, and after it had been rolled while hot, one part was elongated to 16 mm ϕ , and was then ready for the experiment. For the B- and C-orders,

/1473

We used a 50 kg high-frequency furnace for both. With B, we poured off and separated the 50 kg into 10 kg ingots, and made slight changes in the composition; we used C as a 50 kg ingot. In each case, elongation was effected to 15 mm ϕ . Melting was performed at 1100° C; after sustaining this for an hour, it was "water-softened". Part of the steels in the C-order was kept at 1200° C for an hour, and then given "water-softening" treatment. After melting, creep rupture experiments were performed at temperatures of 600° C - 800° C, and with TN5 steel, a high temperature stretching experiment was also performed. The stretching speeds of the high-temperature stretching experiment were the crosshead speeds. Up to 0.2% endurance, it was 1 mm/min; beyond that, it was 5 mm/min. As a parallel part of the experiment, we used on 30 mm, with a diameter of 6.0 mm.

Observation of the structure after creep rupture was performed with a 150 kV electron microscope by means of the extract replica method. The extract replica is formed, in the first step, by using a Birrer solution and, in the second, a 10% bromine-alcohol solution. For the simultaneous fixing of the extract carbides, we relied principally on the analysis of the electron diffraction image, but we confirmed this in part of the samples with x-ray analysis of the residue from an electrolytic extraction accomplished with a 10% solution of hydrochloric acid and alcohol.

We measured the size of the precipitated carbides by means of the electron-microscope photographs of the extract replica. We sought the average values of the length and width of the extract carbide, and established the diameter of a single carbide. We then measured the diameter of the carbide through 10 fields of vision, and with the arithmetical mean of these, we established the average particle diameter of the precipitated material in the steel.

3. Experimental Results

3.1. Differences, based on charge, in the rupture strength of 304H steel

3.1.1. Creep-rupture strength

Figure 1 shows the creep rupture strength curves of Ch. A and Ch. B, at 600° C, 650° C, and 700° C. Considering the rupture strength of both these steels at 650° C 1000 hrs on this chart, we see that Ch. A is

about 10.5 kg/mm², and Ch B is about 14.5

kg/mm². Ch B shows a conspicuously high rupture strength, compared with Ch. A.

Furthermore, in comparing the gradients of the creep-rupture curves of both steels,

we see that Ch. A has a gentler slope. If we extrapolate that,

just as it is, in a straight line, and estimate the rupture strength at 10⁵ hrs, Ch. A has, at 650° C, about 5 kg/mm², and Ch. B — about 9 kg/mm². Furthermore, the estimated rupture strength of Ch. A at 600° C for 10⁵ hrs is about 8 kg/mm². If we compare this with the estimated rupture strength of 9 kg/mm² of Ch. B at 650° C for 10⁵ hrs, we see that Ch. B can be used to a temperature of 50° C higher.

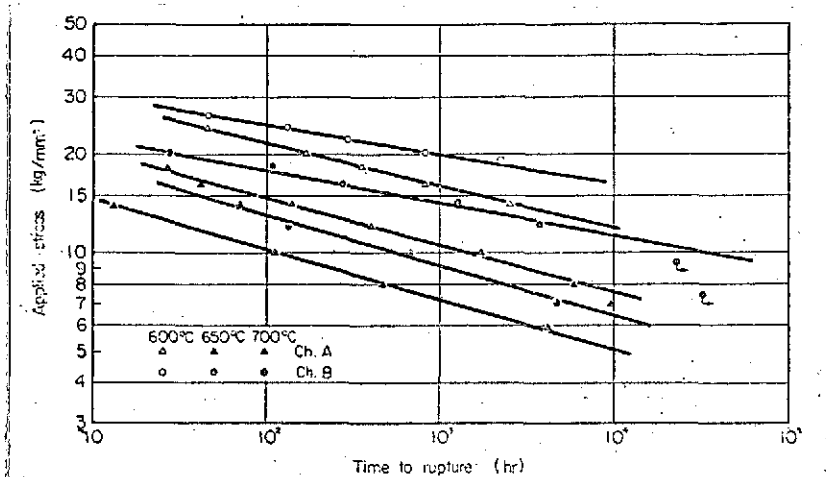


Figure 1. Creep-rupture curves of type 304H steels

/1474

3.1.2. Structure after creep rupture

We have several examples of what we observed in the electron microscope of test samples which ruptured in a relatively short time at 600° C. Ch. A is shown in Photo 1, (a) and (b), and Ch. B in Photo 1, (c) and (d). As to the precipitated carbides of the grain boundary, both steels

show the manner of precipitation of grain-boundary reaction, as can be seen in Photo 1, (a) and (c). If we compare both steels, there are fewer precipitated carbides of this variety in Ch. B than those in Ch. A. As to the forms of the precipitated carbides within the grain, most all are granular in shape. One can see the fine distribution of these in Photo 1,

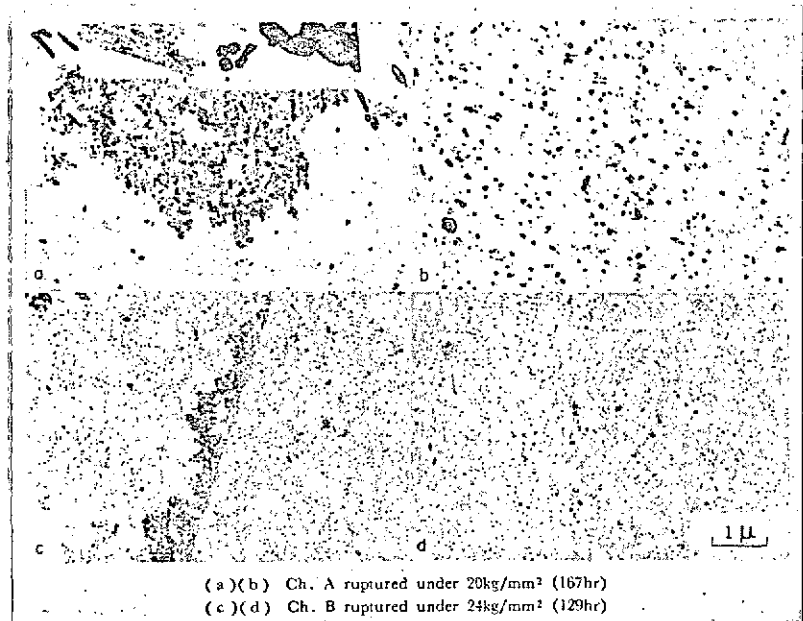


Photo 1. Electron microstructure of type 304H austenitic steels creep-ruptured at 600° C

(b) and (d). There are clear differences in size in the carbides within the grain of Ch. A and Ch. B. In contrast to the average particle diameter of Ch. A, of 0.07 μ , that of Ch. B is about 0.03 μ .

For examples of the replica structure of ruptured material after a long period of time at 600° C, Photo 2, (a) and (b), shows, respectively, the grain boundary and grain interior carbides of Ch. A, and Photo 2, (c) and (d), shows these same carbides for Ch. B. With regard to the sample of Ch. A ruptured at 2611.5 hours, Photo 2 (a) clearly shows that the grain boundary carbides have coalesced, and there is less precipitation of grain boundary reactions, but the precipitation carbides have grown larger. Within the grain, as

Photo 2 (b) shows, we can recognize uniformly distributed carbides. Photo 2 (c) shows what happened with Ch. B, which ruptured at 2251 hours. At the grain boundary, there are many slender, stick-like carbides and fewer carbides of the grain boundary reaction form. The grain-interior carbides, one may see from Photo 2 (d), are extremely fine and evenly distributed. When we compare the precipitation forms of the carbides inside the grain of both steels, Ch. A is clearly the coarser. But with both steels, as is shown in Photo 1, they are the same in size as the carbides precipitated inside the grain of the sample ruptured after a short period. One can hardly recognize changes based on the rupture times.

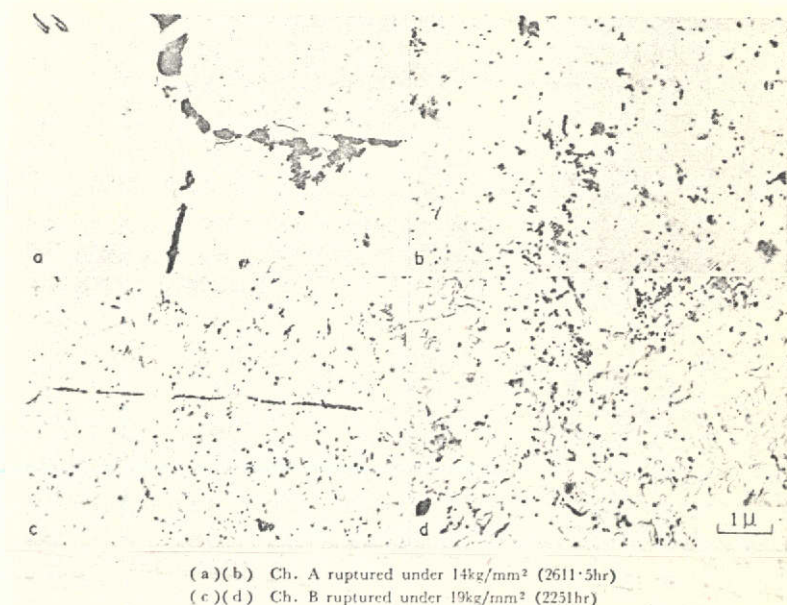


Photo 2. Electron microstructures of type 304H austenitic steels creep ruptured at 600° C

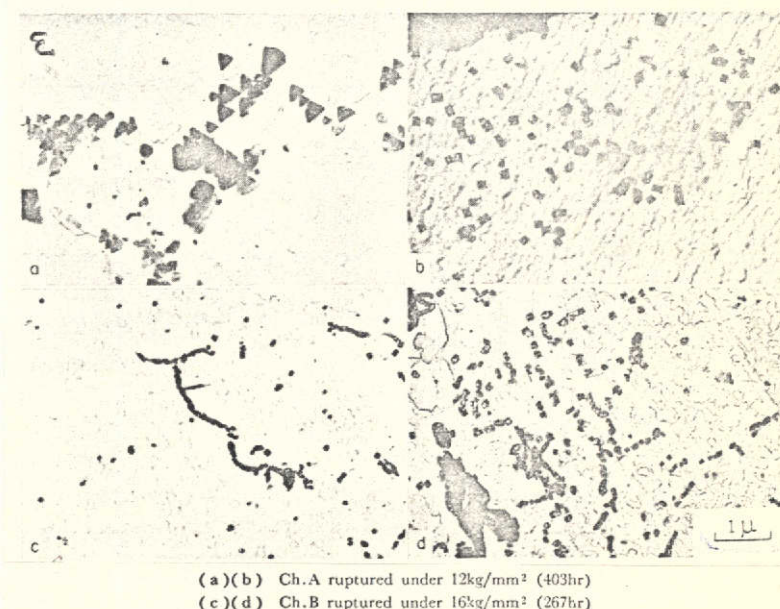


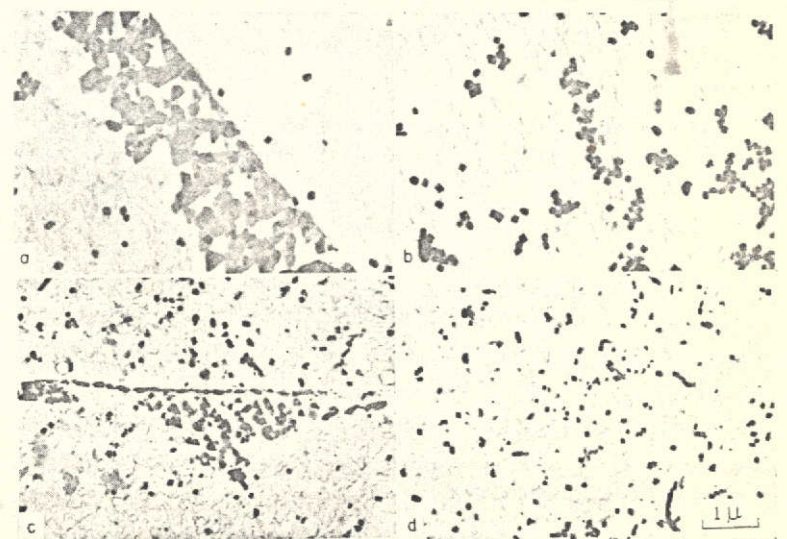
Photo 3. Electron microstructures of type 304H austenitic steel creep ruptured at 650° C

We have shown an example of the replica structure of a sample ruptured in a short time at 650° C. The grain boundary carbides of

the Ch. A sample ruptured at 403 hours are triangular in shape, as in Photo 3 (a), and form a precipitation pattern of the grain boundary reaction-form. The precipitated material of the grain interior, as shown in Photo 3 (b) is chiefly quadrilateral, with an average particle diameter of about 0.14μ . In the case of the Ch. B sample ruptured at 267 hours, the average particle diameter of the grain-interior carbides, compared with that of Ch. A, is smaller, as can be seen in Photo 3, (c) and (d), about 0.08μ . Coalescence of the grain-boundary carbides is slight, but perceptible, and one can observe in Photo 3 (c) the linking of quadrilateral carbides into several strings of beads. M. H. Lewis and B. Hattersley [3] have explained that, when $M_{23}C_6$ precipitates, the quadrilateral forms link, corner to corner and, after rearrangement, precipitate and become Stringer forms. The strung-together carbides, which can be recognized in Photo 3 (c), may be regarded as the same as those of the Stringer form of Lewis et al.

There is some dispute as to the solid form of the carbide $M_{23}C_6$, which can be recognized as trilateral and quadrilateral in electron microscope observations. The above-mentioned Lewis et al. have postulated a multi-faceted shape, whereas F. B. Beckitt et al. [4] have described it as cubical, formed from $\{111\}$ and $\{110\}$ facets.

In Photo 4, we show several examples of the structure of samples ruptured after a long period of time at 650°C . Photo 4 (a)



(a)(b) Ch. A ruptured under 10 kg/mm^2 (1782 hr)
(c)(d) Ch. B ruptured under 14 kg/mm^2 (1286 hr)

Photo 4. Electron microstructures of type 304H austenitic steels creep ruptured at 650°C

shows a Ch. A sample, ruptured at 1782 hours. At the grain boundary it shows a precipitation form of the grain-boundary reaction-form. Within the grain, as in Photo 4 (b), it presents a granular form (quadrilateral form), and the particle diameters average about 0.15μ , which is about the same as the average particle diameter of the sample ruptured at 403 hours — almost no growth at all. With the Ch. B sample ruptured at 1286 hours — one can see this in Photo 4 (c) — there is no indication of a conspicuous grain-boundary reaction-form, as in Ch. A, at the grain boundary; and there is a precipitation of granular carbides. Within the grain, the granular carbides, as one can see in Photo 4 (d), are uniformly distributed; their average particle diameter is 0.10μ .

In Photo 5 we show examples of the structure of Ch. B material, ruptured at 4723 hours at 700°C . Photo 5 (a) and (b) shows the situation of the precipitated carbides within the grain; at 600°C and 650°C , they have not grown to a size large enough to recognize. The average particle diameter of these carbides is 0.3μ . At

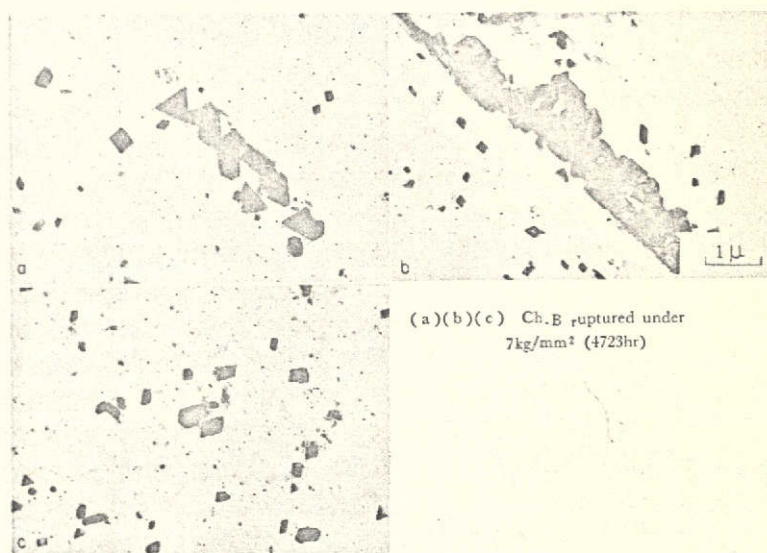


Photo 5. Electron microstructures of type 304H austenitic steel creep-ruptured at 700°C

the grain boundary, grain-boundary reaction-form precipitation is slight, as Photo 5 (c) shows, and we can observe carbides which have developed enormously at the grain boundary.

As shown above, clear differences between the two steels arise upon examining comparatively the precipitation-distribution patterns of the carbides of the two steels, in cases where the rupture times at each temperature are almost equal. That is to say, with Ch. A,

carbide precipitation occurs at the grain boundary and within the grain, at each temperature. Precipitation at the grain boundary is particularly heavy. Grain boundary reaction-form precipitation is conspicuous, and even further coalescence takes place easily. With precipitation patterns such as these, we probably cannot expect that, at the same time grain boundary strength goes down, the strength of the grain interior will increase because of the distribution of carbides. In order to improve high temperature strength, particularly creep rupture strength, it is necessary that there be an effective distribution of the precipitation carbides. It is assumed that an improvement in strength will result when grain boundary reaction-form precipitation is suppressed, and the lowering of the grain boundary strength reduced; when a more uniform distribution within the grain of the carbides which precipitate is affected; and when the re-arrangement-movement which occurs during creep is curtailed by means of the precipitation particles. In investigating Ch. B from the } above standpoint, we find that, in comparison with Ch. A, grain-boundary reaction-form precipitation is less, and the precipitation carbide within the grain is fine and, moreover, uniform. It is possible to assume that one of the principle factors which cause great differences in the creep rupture strength of both steels is to be found in the differences in the precipitation pattern of carbides, such as we have described.

3.1.3. Identification of the carbides which precipitate in 304H steel

We identified the carbide varieties which precipitate in 304H steel, and show the results in Photo 6. In Photo 6 (a), $M_{23}C_6$ was identified from the results of an analysis of an electron diffraction image of the precipitation carbide in the Ch. A extract replica, shown in Photo 3 (b). Photo 6 (b) shows the results of subjecting the electrolytical extraction residue of a Ch. B sample ruptured at 650° at 1286 hours, to x-ray diffraction. An analysis of these results reveals that all the carbide is $M_{23}C_6$. The fact that the carbide which precipitates in 304H steel is $M_{23}C_6$ only has been confirmed

by many researchers [5]. The results of this experiment, too, conform with theirs.

3.2. The effects of small quantities of elements on the creep rupture strength of type 304H stainless steel

In considering the reasons for the differences in the precipitation-distribution patterns of carbides, such as were described in the preceding section, a number of factors can be cited: first, the chemical composition and heat treatment containing small quantities of impure elements, and the degree of crystallization, which is governed by them. Of these, we may consider that there are no great differences, for both Ch. A and Ch. B, with regard to heat treatment and degree of crystallization. Consequently, the problem may be narrowed down to chemical composition, but, as Table 1 shows, the difference in analytical values between the two steels is comparatively slight, and cannot explain the above-mentioned large differences in strength. Even so, it is possible for the time being to assume that, as each of the elements — Mo, Ti, Nb, etc. — is an element in strong carbide formation, each connects with a quantity of C, whether the amount included is small or not, and has the possibility of causing tremendous changes in the precipitation-distribution pattern of the carbides. It is known [6] that N delays the coalescence of carbides. For this reason, we first investigated the effects which the addition of these elements in small, separate

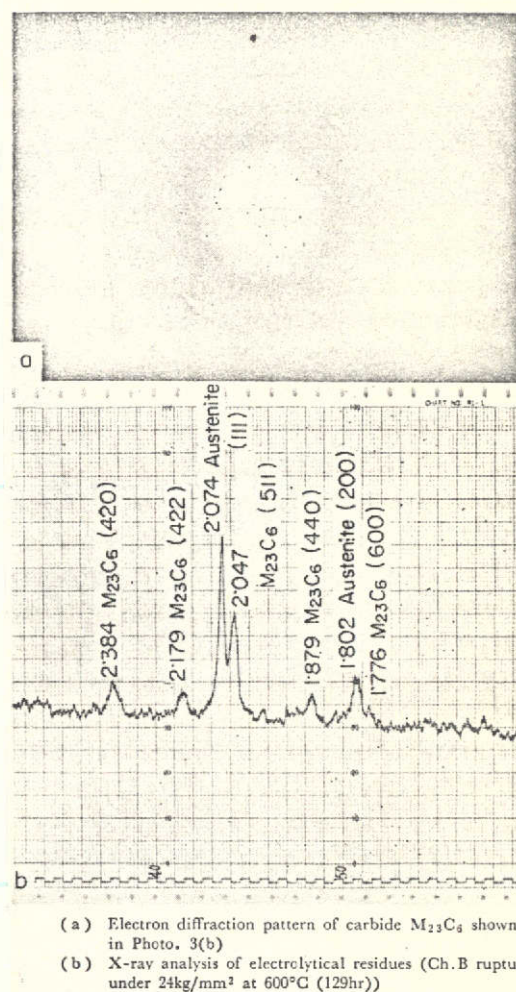


Photo 6. Identification of $M_{23}C_6$ precipitated in creep ruptured specimens of type 304H austenitic steel

quantities had on the creep rupture strength of type 304 steel. From the results, we selected the elements considered to be strong factors in accounting for the difference in strength between Ch. A and Ch. B. We went even further, for we carried out a detailed investigation which covered the influence that the precipitation pattern of the carbide had.

3.2.1. The effects of C

With regard to the effects that C has on creep rupture strength, Nakagawa et al. [7] added C to the extent of 0.12% in 18Cr-12Ni steel and performed creep rupture experiments at 650° C and 700° C. They showed that, depending on the amount of C added, the creep rupture strength is considerably increased. For this reasons, the authors also cast steel containing C from 0.03% to 0.23%, and studied the relationship between the amount of C and the creep rupture strength.

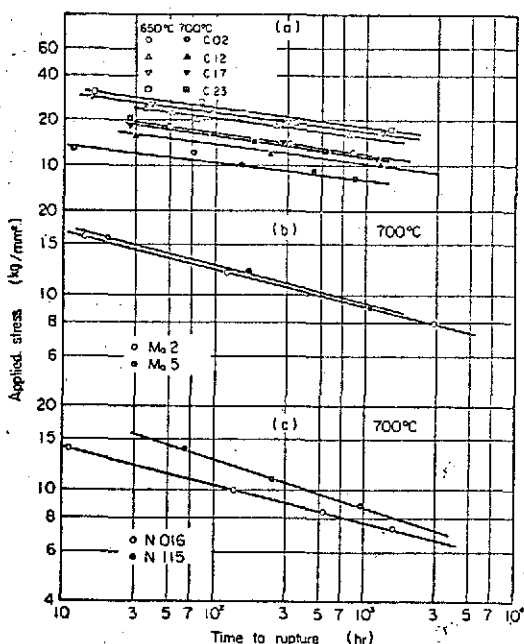


Figure 2. Effects of C, Mo, and N on the creep rupture strengths of type 304 austenitic steel.

Figure 2 (a) shows the creep rupture curves at 650° C and 700° C, which were obtained for steels C02-C23 of Table 1. And Figure 3 shows the relationship between the amount of C, the 100 hour creep

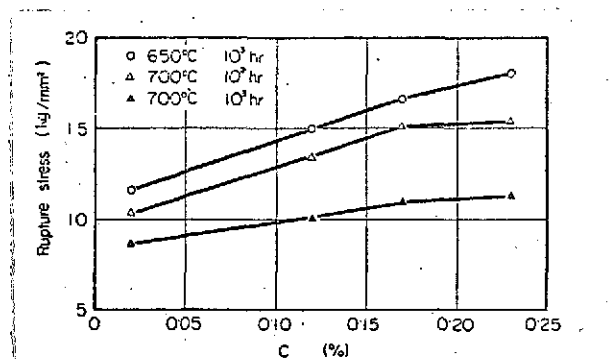


Figure 3. Relation between carbon content and rupture stress of type 304 austenitic steels at 650° C and 750° C

rupture strength at 700° C, and the 1000 hour creep-rupture strength for both temperatures, as obtained from the figure just mentioned. /1477 Together with the amount of C, the creep rupture strength clearly increases. It increases to 0.3 kg/mm² within the range of C 0.02 - 0.17%, and at C 0.01% for the 1000 hour creep rupture at 650° C and 700° C. On the other hand, even when the difference in C content for Ch. A and Ch. B, mentioned above, is as little as 0.02%, the 1000 hour creep rupture strength is about 4.0 kg/mm² at 650° C, and 1.8 kg/mm² at 700° C. Compared with the above-described effects of C alone (converting to 0.02% C, 0.6 kg/mm² at 650° C and 700° C), at 650° C, the change is about 6.6 times; and at 700° C — 3.0 times. Consequently, it is difficult to believe from the difference in strength between Ch. A and Ch. B that this effect solely results from a mere 0.02% difference in C.

3.2.2. The effects of Mo

Nakagawa et al. [8] also report on the effects of Mo on the creep rupture strength of 18Cr-12Ni steel. They changed Mo to a range of 0.85% - 3.5%, setting up a relationship with the C content, and studied the efficacy of Mo. They reported in particular that, in the case of high C content, the strengthening behavior of Mo is very pronounced. But they did not investigate what happens when small amounts below 0.85% are added. The difference in Mo content between Ch. A and Ch. B in the present experiment is 0.32%, and so it is necessary to study the effects on creep strength of Mo in amounts below 0.5%. Therefore, we cast Mo2 steel which contained 0.24% Mo, and Mo5 steel, which contained 0.53% Mo, and plotted in Figure 2 (b) their creep rupture curves at 700° C. It is clear from these results that the effect of Mo below 0.53% on creep rupture strength at 700° C is almost imperceptible. It is difficult to /1478 believe, therefore, that the difference in strength between Ch. A and Ch. B which occurs is due to the influence of Mo at 0.32%.

3.2.3. Effects of N

It has been reported [9] by many researchers that the high temperature strength of austenitic steel is improved with the addition of N. There are also reports [6] to the effect that N, when it co-exists with C, prevents the coarsening of the precipitation carbides, and that creep rupture strength improves. But the amounts of N in Ch. A and Ch. B are, respectively, 0.0273% and 0.0472%; the difference between them is a mere 0.02% or so. It is not clear how such small amounts of N affect the creep rupture strength. Therefore, to study the effects of N by itself, we compared the creep rupture strength, at 700° C, of N016 steel, which contains 0.0164% N, and of N115 steel, which contains 0.1154% N. The creep rupture curves of these two steels are shown in Figure 2 (c). From this chart, it is clear that an increase in N causes considerable strengthening. Only two different kinds of steels are involved in these results, but if we hypothesized that the changes of N between 0.0164% and 0.1154% caused the creep rupture strength to change in a straight line, we would expect that the increase in 1000 hour creep rupture strength, where N was in the neighborhood of 0.01%, would be about 0.1 kg/mm². With a difference of 0.02% in N% between Ch. A and Ch. B, we would see a strengthening to the extent of 0.2 kg/mm². But, in actuality, the difference in the 1000 hour rupture strengths at 700° C between Ch. A and Ch. B is 1.8 kg/mm². Compared with the 0.2 kg/mm², there is a nine-fold increase in strength, making it hard to believe that N alone brought about the differences in strength between the two steels.

3.2.4. Effects of Ti and Nb

There are a few reports on the effects of Ti [10] and Nb [7] on the creep rupture strength of 18Cr-12Ni-line austenitic steel, but each of these studies made use of steels with comparatively large amounts of Ti and Nb additives. In particular, they state values of Ti/C and Nb/C above 3, and leave entirely unstudied the

influence of small amounts of Ti or Nb in the vicinity of 0.1%, or as in the Ch. B of our research.

Therefore, the authors first sought the creep rupture curve for T02 steel, containing 0.02% Ti, and for steel containing Nb at 0.34%, the result being shown in Figure 4 (a). We used Figure 3 through interpolation to find the rupture strength where C is 0.14%, and we show this in Figure 4 (a) with a dotted line. From this chart, the 700° C 1000 hour rupture strength of T02 steel is about 9.2 kg/mm², but C12 steel, which has the same C content (0.12%) as T02 steel but does not include Ti, is about

10.0 kg/mm². The strength is lowered with Ti added. Furthermore, the 700° C 1000 hour rupture strength of NB 34 steel is about 10.6 kg/mm². But the projected 1000 hour rupture strength of

steel containing C at 0.14% is about 10.4 kg/mm²; and even with the addition of 0.34% Nb, the rupture strength is almost unchanged. From these results, it is difficult to believe that, as compared with Ch. A, a far superior strength will be produced through either 0.014% Ti or 0.003% Nb, included separately in Ch. B.

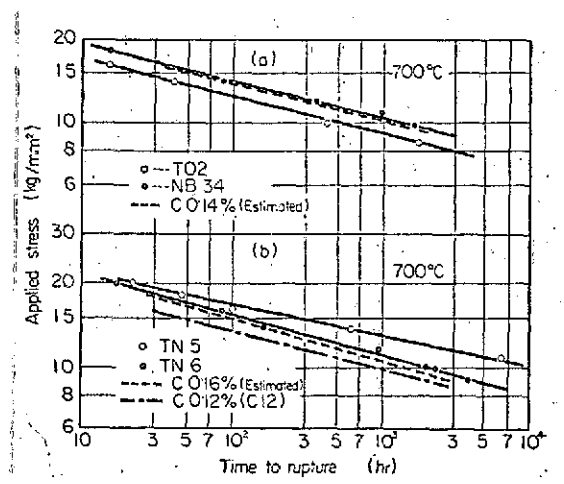


Figure 4. Effects of Ti, Nb and Ti + Nb on the creep rupture strengths of type 304 austenitic steel at 700° C

3.2.5. Effect of simultaneous inclusion of Ti and Nb

We investigated above the case of single additives of various elements, but we will now describe, as an instance of compound addition, the far greater efficacy that resulted when a simultaneous addition of Ti and Nb was made.

We show in Figure 4 (b) the creep rupture curve at 700° C of TN5 and TN6 steels, which include small amounts of Ti and Nb. Also shown on the chart with a dotted line is the creep rupture curve, hypothesized from Figure 3, where the C content is the same as TN5 steel; and, with the dash-dot line, the case of C12 steel (0.12% C), which has a C content the same as TN6 steel. In contrast to a 1000 hour rupture strength of 13.3 kg/mm² in TN5 steel, the projected rupture strength of 0.16% C which does not include Ti and Nb is 10.8 kg/mm² and when Ti and Nb are included it is 2.5 kg/mm². And in contrast to the 11.2 kg/mm² of TN6 steel, the 10.0 kg/mm² of C12 steel represents a rise in strength of 1.2 kg/mm². Moreover, when we compare TN5 steel and TN6 steel, the improvement in strength is 2 times, with only slight changes of Ti 0.07% and Nb 0.03%. It is clear that creep rupture strength is significantly affected by small amounts of Ti and Nb.

Nevertheless, it is dangerous to conclude on the strength of the above results alone that differences in strength between Ch. A and Ch. B are unmistakably due to the presence of small quantities of Ti and Nb. It is probably more reasonable to interpret the differences in strength that occur as the result of C, Mo, N, etc., complicating the process. As we explain later on, a finer precipitation and uniform distribution of carbides occur in steel containing small amounts of Ti and Nb, and, because of this, differences in the strengths of the steel arise from the differences in the patterns of the precipitated carbides. Therefore, what is important is the presence of small amounts of Ti and Nb, which is responsible for the change in pattern. /1479

3.3. Type 304 steel to which small amounts of Ti and Nb have been added

In the previous section, we made clear how the simultaneous addition of small amounts of Ti and Nb brings an improvement in creep rupture strength. It is necessary to include further a study regarding the correct values of the added amounts of Ti and Nb, and a study of the effects of Ti + Nb on the precipitation patterns of carbides.

3.3.1. Creep rupture characteristics

The creep rupture curves for TN1 - TN7 steels, which include small amount of Ti and Nb, are shown in Figures 5 - 9. The TN1 steel shown in Figure 5 has had, to a low C content of C 0.03%, an addition of Ti 0.10% and Nb 0.18%, but compared with Ch. B, it shows strength that is equivalent or somewhat higher. The TN2 steel of Figure 6 has had, to a 0.14% C, additions of 0.43% Mo, 0.12% Ti, and 0.34% Nb. It has already been related how the differences in strength between Ch. A and Ch. B are not the result of Mo efficacy alone. In order to study whether there is or is not an interaction between small amounts of Ti and Nb and Mo, we compared TN2 steel and TN3, which latter is shown in Figure 7. TN2 steel has a 1000 hour rupture strength at 650°C of

18.0 kg/mm², while TN3 steel had 17.8 kg/mm². TN2 steel had a slightly higher value. It is safe to say that even adding Mo at 0.43% to the small amounts of Ti and Nb had almost no effect. From the above results, we may consider that the presence of Mo in the range of 0.4% contri-

butes almost nothing to the strength, but that the strength may be effectively raised with the two elements, Ti and Nb.

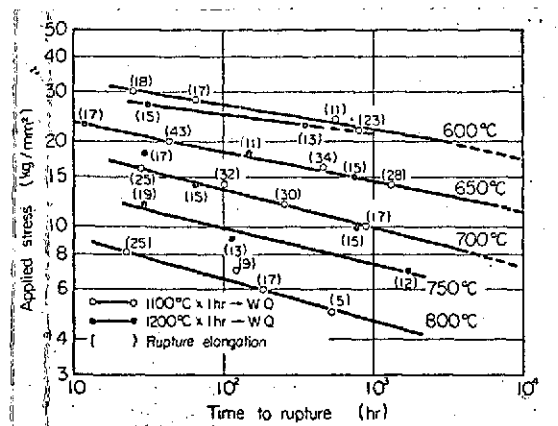


Figure 5. Creep rupture curves of TN1 steel

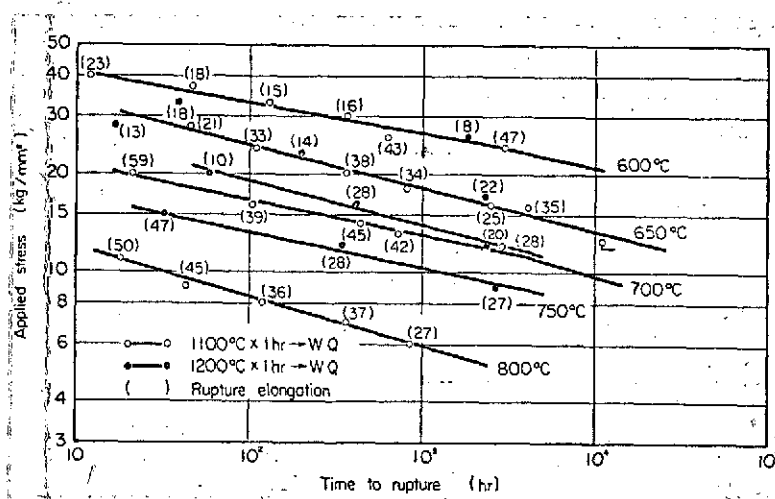


Figure 6. Creep rupture curves of TN2 steel

The TN4 steel shown in Figure 7 contains, in addition to 0.16% C, 0.08% Ti and 0.30% Nb. Compared with TN3, there is an improvement of 1 kg/mm² at a 650° C, 1000 hour rupture strength.

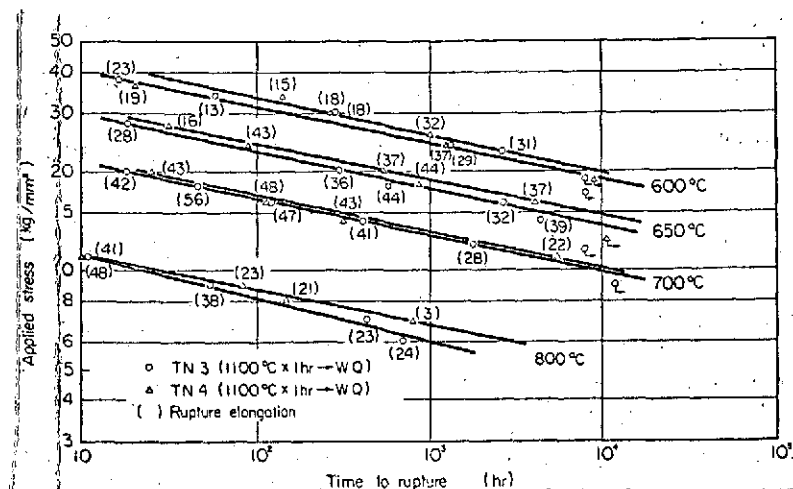


Figure 7. Creep rupture curves of TN3 and TN4 steels

In comparing TN5 steel, melted at 1100° C and shown in Figure 8, with TN4 steel, the difference in the 650° C 1000 hour rupture strengths is a mere 0.5 kg/mm², but at a 10,000 hour projected rupture strength (using a method [11] proposed by one of the authors) — 1.5 kg/mm²; and at a 700° C 1000 hour rupture strength, a difference

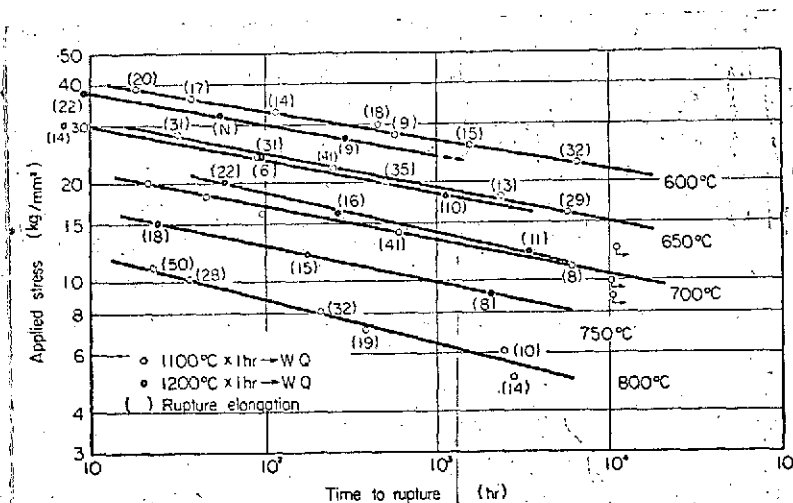


Figure 8. Creep rupture curves of TN5 steel

of 1 kg/mm² was recognizable. In comparison with the TN4 steel, the amount of Nb is about one-half, yet the slope of the creep-rupture curve is gentle, and the long period rupture strength has risen. /1480

The TN6 and TN7 steels shown in Figure 9 both have a lower rupture strength than TN5 steels. The C of these two steels is 0.12%, and the Ti is 0.02% and 0.03%, practically uniform. The Nb in TN6 is 0.10%, compared with 0.02% in TN7. But the 650° C, 1000 hour

rupture strength of TN6 steel is 17.0 kg/mm²; by contrast, TN7 steel has 14.7 kg/mm², about 2 kg/mm² lower.

With regard to the influence of the melting temperature on creep rupture

strength, we studied this using TN1, TN2, and TN5 steels. With TN1 melted at 1200° C, the rupture strength at 600° C was a little lower than for material melted at 1100° C. There was almost no difference between the two, at 650° C and 700° C. With TN5 steel, a slight difference was observable between the material melted at 1100° C and that at 1200° C. At 600° C, the rupture strength of the material melted at 1100° C was higher; at 650° C, both showed almost the same strength. At 700° C, the material melted at 1200° C was stronger on the short period side, and the slope sharper. However, the creep rupture curve of the material melted at 1200° C was superimposed practically on top of the same curve for the material melted at 1100° C, on the long period side. Presumably, the influence of the melting temperature is felt only on the short period side. Information on rupture elongation is appended in the respective charts, but steels containing small amounts of Ti and Nb, when compared [1] with steels 321 and 347, show better values.

The steels used in this experiment containing Ti and Nb are considered to improve the creep rupture strength by means of the interaction between Ti and Nb, and C. But since all the steels have different C content, we sought the connection between the C content and the 700° C, 1000 hour rupture strength, and give the results in Figure 10. As a comparison with steels that do not contain Ti and Nb, we reproduced material from Figure 3. According to the chart,

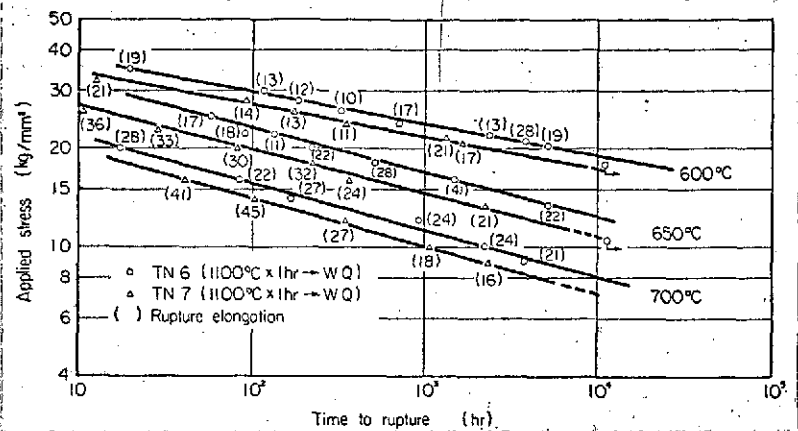


Figure 9. Creep rupture curves of TN6 and TN7 steels

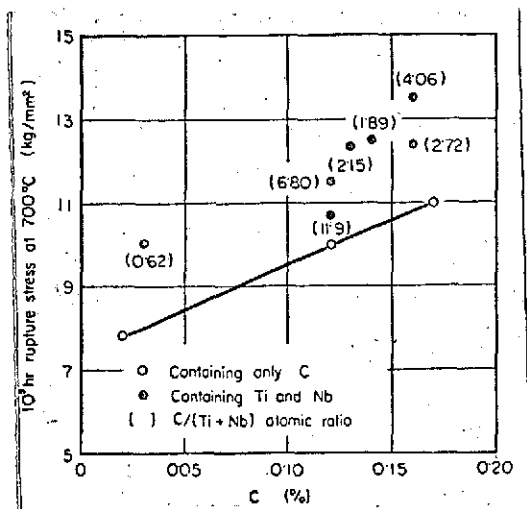


Figure 10. Relation between carbon contents and 10^3 hour rupture stress of type 304 containing Ti and Nb at 700°C

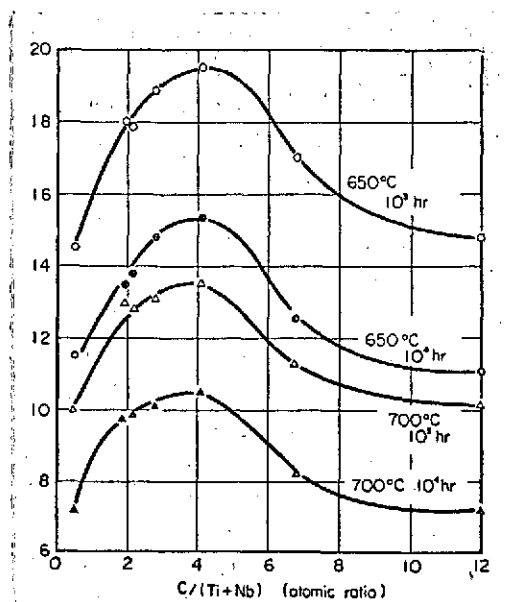


Figure 11. Relation between 10^3 and 10^4 hour rupture stress and atomic ratio $C/(Ti + Nb)$ at 650°C and 700°C

C content and strength both rise in a straight line in steels not containing Ti and Nb. And in steels containing Ti and Nb, there is, in general, a tendency for an increase in C content to be accompanied by one in strength, but the scatter is fairly large, and we cannot resolve the issue by C content alone. That is, we presume that some factor other than C content is involved. Therefore, we sought the relationship between the atomic ratio $C/(Ti + Nb)$ and rupture strength and obtained Figure 11. What is clear from the Figure is that the atomic ratio $C/(Ti + Nb)$ is in the vicinity of 4, and the creep rupture strength shows an extremely high value. The steel where $C/(Ti + Nb)$ is near 4 is TN5, but with this steel, as we have said, the slope of the creep rupture curve is gentle, and the projected long period rupture strength is high. /1481

3.3.2. Comparison of the creep rupture strength of TN5 steel with those of other steels

Figure 12 shows a comparison of the creep rupture strength of TN5 steel with that of 304H and 316H stainless steels used as piping

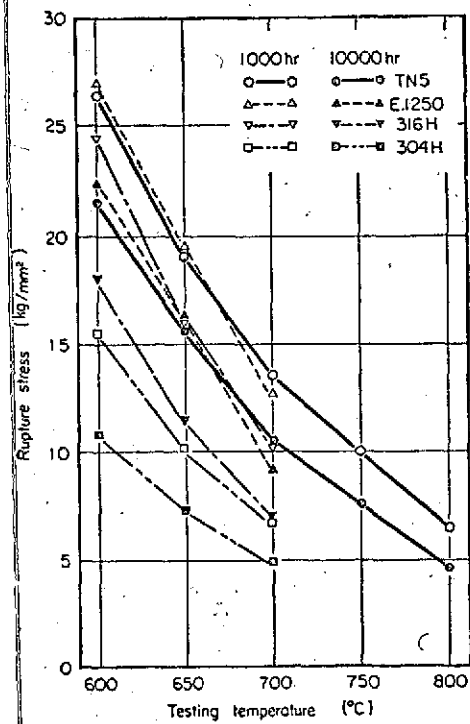


Figure 12. Comparison of the creep rupture strength of TN5 steel with commercial austenitic steels

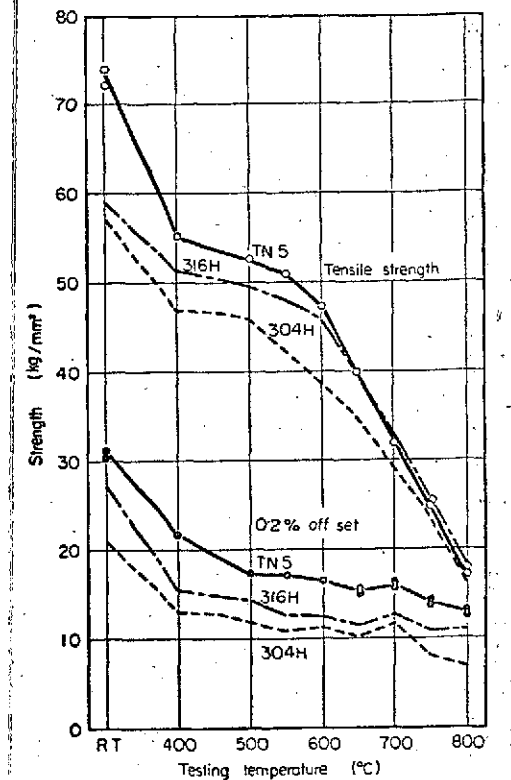


Figure 13. Results of the high temperature tensile tests of TN5 steel

in currently used representative boilers and those of Esshete 1250 [12], which was developed in England. The values of Esshete 1250 steel displayed the lower limit values of the data band which is shown in the literature [12]. It goes without saying that TN5 steel has a higher strength than 304H. The projected 700° C 10,000 hour rupture strength of TN5 steel was equal to the 650° C 10,000 hour rupture strength of 316H. Consequently, the former, in comparison with 316H steel, can be used at temperatures 50° C higher. Compared with Esshete 1250, it hardly reaches at 600° C and 650° C; but at 700° C, TN5 shows a higher value than the lower limit of the Esshete 1250 band. In particular, the rupture strength of Esshete 1250 falls off rapidly after 700° C, 30,000 hours, but with TN5, if we extrapolate [11] the 700° C long period rupture strength from the 750° C and 800° C creep rupture curves, one may predict that there is no such rapid fall-off of strength, as with Esshete 1250, and that it will maintain comparatively high strength until 10^5 hours.

/1482

3.3.3. High temperature tensile characteristics of TN5 steel

Figure 13 shows the results of high temperature tensile testing of TN5 steel, which has a high creep rupture strength. For the sake of comparison, other representative austenitic steels were tested. Results regarding the samples of 304H and 316H, melted at 1100° C, are therefore also shown in the figure. The tensile strength of TN5 at normal temperatures is unusually high, at about 72 kg/mm²; compared with those of 304H and 316H, it is about 10 kg/mm² stronger. This is mainly thought to arise from the high content of carbon. If we compare the high temperature tensile strength with that of 304H steel, TN5 is higher, up to 800° C; even compared with 316H, TN5 shows higher tensile strength up to 650° C, but beyond that the three steels show practically the same values.

Under 0.2% stress, TN5 is far higher than 304H, and it is superior by 20%, even when compared with 316H.

Stretch at normal temperatures is about 60%, and by 500° C declines to about 40%; but above 600° C, it increases. At 800° C, it once again shows a value in the range of 60%.

3.3.4. Structure of TN5 steel after creep rupture

Photo 7 shows several examples of creep ruptured test material of high rupture strength TN5 steel, as observed through the electron microscope. In Photo 7 (a), a carbide precipitation at the grain boundary is observable in the 600° C 18 hour ruptured material, but within the grain, carbides may barely be seen. The rupture time lengthens, and at 2400 hours, fine grain carbides precipitate uniformly within the grain, as in Photo 7 (b), with the average particle diameter being about 0.05 μ . The grain boundaries are almost no different from those of the 18 hour ruptured material, even though they underwent the long period creep changes. Consequently, one does not see precipitation of the grain-boundary reaction-form, such as

seen in 304H steel. For 650° C, as Photo 7 (c) shows, a fine carbide precipitates within the grain in the 90 hour ruptured material; there is, as expected, no sign of the grain boundary reaction-form carbide pattern. As Photo 7 (d) shows, in the 2400 hour ruptured material, the carbides coalesce more than they do in the 90 hour ruptured material; the average particle diameter of 0.07 μ . However, in comparing Photos 4 (c) and (d), it is clear that the grain interior carbides of TN5 steel are smaller.

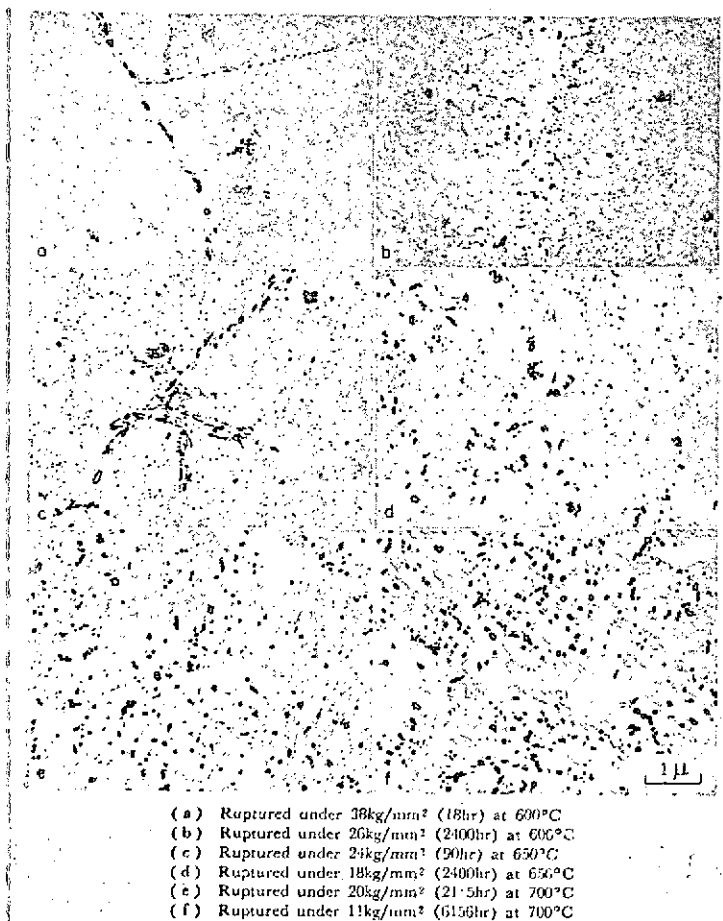


Photo 7. Electron microstructures of creep ruptured TN5 steel after solution treatment at 1100° C

At 700° C, the 21.5 hour ruptured material, shown in Photo 7 (e), has an average particle diameter of 0.05 μ , and the 6156 hour ruptured material of Photo 7 (f) has 0.1 μ . In contrast to the average particle diameter of 0.1 μ in the carbides formed of Ch. B at 650° C for about 1000 hours, TN5 steel has the same 0.1 μ at 700° C, above 6000 hours. This shows that the structural stability is remarkably superior in TN5 steel at high temperatures when the right amounts of Ti and Nb are present. And even at 700° C, TN5 steel revealed almost no sign of the grain boundary reaction-form carbide pattern, which appeared in the Ch. B steel.

We show in Photo 8 how the size of the grain-interior precipitated carbides change, based on the value of $C/(Ti + Nb)$. Photo 8 (a) shows the TN6 sample ruptured at 650° C, 5210 hours

[$C/(Ti + Nb) = 6.8$]. Compared with the TN5 material ruptured at 2400 hours [Photo 7 (d)], the average particle diameter is large, having become 0.08μ , but it is smaller than the 0.15μ of the Ch. A sample ruptured at 1782 hours [Photo 4 (b)]. At $700^\circ C$, the TN3 [$C/(Ti + Nb) = 2.1$] sample ruptured at 1738

hours has an average particle diameter of 0.18μ . Compared with the TN5 sample ruptured at 6156 hours, larger carbides have precipitated, in spite of the shorter rupture time. But compared with the Ch. B sample ruptured at 4723 hours, the TN3 has finer carbide.

From the above results, we may assume that small amounts of Ti and Nb cause the precipitation of a finer, more uniform carbide. Moreover, there is an action which delays the coalescence of the carbides; efficacy is greatest when the atomic ratio of $C/(Ti + Nb)$ is near 4.

4. Remarks

4.1. Regarding the scatter of the creep rupture strength of 304H steel

When we analyze the creep rupture data [1] for 304H steel that has been published, it is only in this kind of steel that the scatter based on the rupture strength charge is great. But at similar charges, there is almost no change in strength, even if the heat treatment temperature is changed within a fairly wide range. By contrast, in 316H and 321 steels, the scatter based on the charge is comparatively small if we limit the heat treatment. In Figure 14, we show the results drawn from the ASTM data [1], and compared Ch. A

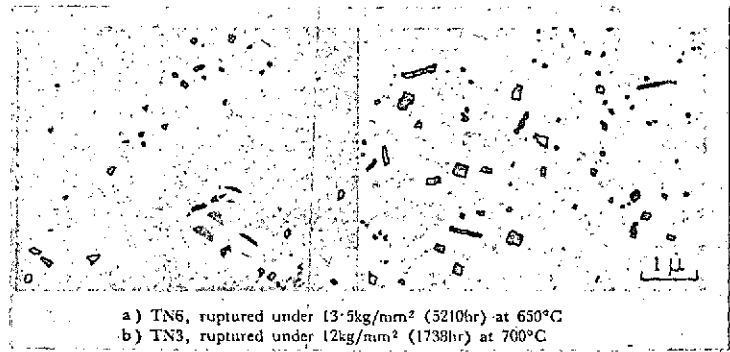


Photo 8. Comparison of carbide precipitated in creep ruptured specimens of type 304 austenitic steels containing Ti and Nb /1483

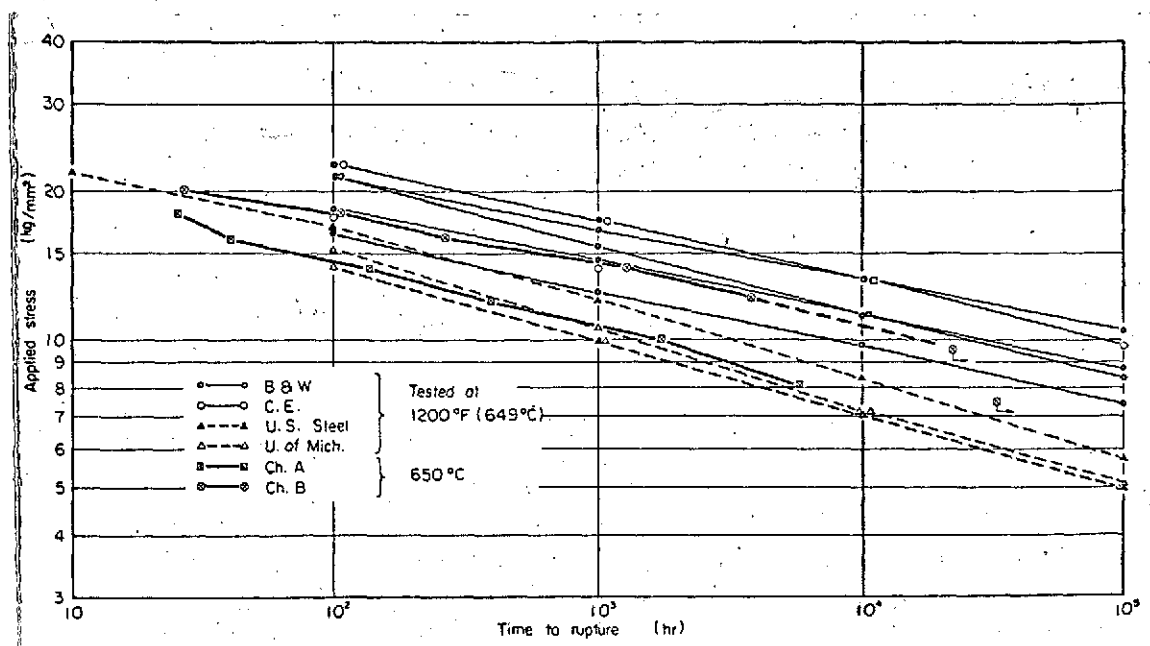


Figure 14. Creep rupture curves of type 304 steels melted by different shops at the testing temperatures of 649° and 650° C

and Ch. B. Among the creep rupture curves, high strength creep occurs with the boilermakers, B & W Co., C. E. Co., etc.; the lower creep with U. S. Steel and the University of Michigan. The thing to be understood from this is that, particularly with universities, etc., the material melted is extremely pure, whereas the B & W, C.E., etc., a high percentage of the material melted was scrap; one may fully expect an admixture of small quantities of Ti, Nb, Mo, N, and other elements. In the authors' case, too, scrap was not used with Ch. A, but with Ch. B, a large quantity was used. Thus, it is possible that there was an admixture of small quantities of the elements.

In the section "Experimental Results", we described the efficacy of single elements. Based on these results, the influence of single elements was not readily evident. Consequently, differences in strength arose owing to the interaction of small quantities of several different elements, and the microstructure was also affected. The results of this experiment show that carbides become finer owing to the interaction of small quantities of Ti and Nb, but we cannot say that this is the result of the interaction of these two elements

/1484

alone. That is, we should consider the elements Mo, N, B, C, etc., along with the extremely small amounts of Ti and Nb. L. M. Hopkins et al. [13] point out that the differences in creep rupture strength of type 316 steel based on the charge are due to the solidification of N and B, but they may assume that the improvement in strength is due to the interaction of Mo and B, or Mo, N, B, C, etc.

Kawabe et al. [14, 15] have reported that adding small amounts of B, Ti, Nb, and other elements to 18Cr-12Ni-3Mo steel resulted in: an improvement in creep rupture strength; a stabilization of the structure, particularly with Ti and Nb; and changes in the precipitation speed of $M_{23}C_6$, in the coalescence speed, and in the carbide patterning. This agrees with the results of our experiment where type 304 steel did not contain Mo.

Tanaka et al. [16] studied the effects of nitrogen and carbon on the high temperature strength of 25Cr-20Ni heat-resistant steel. The increase in creep rupture strength based on the combined addition of C + N was remarkable, and they discovered that their interaction at 800° C was even more pronounced. Moreover, they found that N caused a delay in the coalescence speed of the carbide $Cr_{23}C_6$. One [17] of the authors also, in regard to the interaction of Mo and N, confirmed this where Mo and N were added in larger amounts, with 25Cr-28Ni steel. And Kawabe et al. [18] confirmed the same in 18Cr-12Ni-3Mo steel, where the density of N is comparatively low. They took this as due to the greatly reduced creep speed that resulted, mainly, from the strengthening of $CrMoN_x$ precipitation.

From research results such as those above, one may assume that the 304H steel on the market has a highly variable high temperature strength due to the interaction of small quantities of numerous elements such as Ti, Nb, Mo, N, B, C, etc., that are part of it. But, as we showed with TN2, if we add small quantities of Mo in addition to the small quantities of Ti and Nb, it has very little effect. So the chief reason for the random effect may be very largely the result of the interaction of small quantities of Ti, Nb, and C.

4.2. Amount of Ti and Nb added, and its economic value

We have already related how adding small amounts of Ti and Nb to type 304 steel improves creep rupture strength, and how an atomic ratio of $C/(Ti + Nb)$ in the neighborhood of 4 shows the greatest strength. From this value, if one already knows the amount of C, the proper amount of Ti + Nb can be calculated. However, we have not touched on the proper amounts of Ti and Nb. According to the results [19] of a later experiment, creep rupture strength is the greatest when, where $C/(Ti + Nb) = 4$, the atomic ratio $Ti/(Ti + Nb)$ is between 0.35 - 0.65, but in regards to this, we plan a later report. From this relationship, if we calculate for the case where, say, C is 0.12%, and set $C/(Ti + Nb) = 4$, and $Ti/(Ti + Nb) = 0.5$, we obtain the most superior rupture strength when Ti wt% = 0.06 and Nb wt% = 0.12. Even though the amounts added are slight, we can expect a higher strength than with 316H steel. Thus there is no necessity of using expensive Mo in high quantities of 2 - 3%. The economic value is tremendous.

4.3. Strengthening by addition of small amounts of Ti and Nb

As described above, the addition of small amounts of Ti and Nb improves creep rupture strength; the main reason for this may be assumed to be in the precipitated carbide. As explained in section 3.3.4, a fine carbide is precipitated in uniform distribution in steel (TN5) to which small quantities of Ti and Nb have been added. Furthermore, it was found from observations of the replica structure of samples ruptured at high temperatures over long periods, that the coalescence of the carbides was delayed. A report has already been made regarding changes in structure and in carbide patterning after aging and creep rupture of 304H and 316H steels, which do not include Ti and Nb. It is known that, with long period aging, the coalescence of carbides progresses and that grain boundary reaction-form precipitation is frequent. Reports have also been made regarding changes in the structure of 321 steel [5, 21 - 25], which includes Ti, and

347 steel [5, 24 - 26], which includes Nb; and, in particular, regarding pattern changes in the carbides. Ti and Nb stimulate the precipitation of fine carbides, but in the steels where C is fixed with Ti and Nb, needle-like carbides precipitate on the long period side, and become — as assumed in [5, 25 - 27] — the cause of a lowering in strength. As we have seen, there is a close connection between the pattern of precipitated carbides and high temperature strength. It is assumed that an improvement in high temperature strength can be expected by artificially controlling the precipitated carbides. That is, by causing the carbides to precipitate finely and in a nearly circular condition, and the coalescence of the precipitated carbides to be delayed, high temperature strength should rise through the so-called distribution of carbides. Regarding the function of strengthening carbide distribution, Tanaka [26] reports that with heat-resistant steels and alloys used in industry, mechanisms based on the Suzuki Effect and the I.S. effect are important, but, in addition to these strengthenings, the method of increasing strength by distributing fine carbide over the entire surface of the face fulfills a more important function than strengthening solidification. This was seen in many cases. Among the strengthening mechanisms, we found the important function of distribution strengthening.

Where alloys have been strengthened by distribution, an important factor governing strength is the distance between the distributed particles. McLean [29] and Grant [30] have pointed this out. Ansell [31] and Unckel [32] and others insist that distance alone does not determine strength, but that the size of the particles must be viewed as important as the distance between them.

The case of type 304 steel to which small amounts of Ti and Nb have been added differs from that of distribution strengthened alloys, but it is possible that, in order to secure high strength through carbide distribution, there may be an approach similar to the one employed with distribution strengthened alloys. If we assume that there is a set amount of carbon in the steel and that there is neither decarbonization nor carbonization during aging, there will be a mutual relationship between the size of the carbide particles

/1485

precipitated and the distance between those particles. If the particles are fine, the distance between them will be fine. As was said before, the size of the particles is related to the strength. In terms of experimental technology, the size of the particles may be obtained fairly precisely, from the electron microscope image of the extract replica, far easier than the distance between the particles. It is by no means unreasonable, therefore, to use the average particle diameters as a quantitative yardstick, which will indicate to us the distribution situation. It was from this standpoint that, in this study, we paid close attention, mainly, to the size of the precipitated carbides in the numerous samples of test steel, creep ruptured at a variety of temperatures, and studied in particular the effects of small amounts of Ti and Nb.

We have made it clear that small amounts of Ti and Nb included in type 304 steel cause the fine precipitation of the carbide $M_{23}C_6$ and, further, that they slow down the speed of its coalescence. But it is conceivable that the improvement in strength was brought about through the effects of the distribution of fine carbides. We have already related how the interaction of Ti and Nb, when the atomic ratio of $C/(Ti + Nb)$ is 4, contributes most to the strengthening. However, this indicates the possibility that about three-fourths of the C which remains after about one-fourth of the C becomes fixed in the form of TiC and NbC, because of the presence of Ti and Nb, will precipitate as $M_{23}C_6$. Consequently, it is conceivable that the precipitation of this $M_{23}C_6$, which occurs during creep, is distributed finely and evenly in the grain interior through some type of action with TiC and NbC. To find the reasons for this, further research in detail, using penetrating electron-microscopic observations, etc., is necessary, and is a future problem.

5. Conclusion

After investigating the scatter due to charge of creep rupture strength of 304H steel, and the high temperature strength of type 304 steel to which small amounts of Ti and Nb have been added, we obtained the following results:

1. In 304H steel, the creep rupture strength varied markedly, depending on the charge. The main factors are the carbide precipitation, coalescence, and distribution conditions.

2. The conditions of carbide precipitation, coalescence and distribution are considered to be due principally to the interaction of small quantities of components, like Mo, N, Ti, Nb, C, etc., mixed in. And it is thought that the effects of the interaction of the three constituents, Ti, Nb, and C, are especially great, and important.

3. The simultaneous addition of small quantities of Ti and Nb to type 304 steel makes a marked improvement in high-temperature strength. The greatest strength is shown when the atomic ratio of $C/(Ti + Nb)$ is near 4.

4. Small amounts of Ti and Nb added to type 304 steel cause, at high temperatures, the precipitation of the carbide $M_{23}C_6$ to be finer and more uniform, and they markedly slow down the speed of coalescence and stabilize the structure. The most efficacious action occurs when the atomic ratio of $C/(Ti + Nb)$ is near 4. It is assumed that there will be an improvement in strength with a strengthening of the distribution of the precipitated carbide.

5. In this experiment, the steel (TN5) with the highest strength had a 10,000 hour rupture strength at $600^{\circ}C - 700^{\circ}C$, that was higher than that for 316H steel, and at $700^{\circ}C$, it had a strength to rival Esshete 1250.

6. With type 304 steel to which small amounts of Ti and Nb have been added, the cost of alloying elements is cheaper than that of 316H steel, in which the expensive Mo, at 2 - 3%, is used. Moreover, creep rupture strength is higher; and, economically speaking, it is better.

We would like to express our thanks to Prof. Tanaka Yoshihira of the Engineering Department of Tokyo Industrial University, and our deep thanks to Shigetada Sakai, Chief of Technical Research for Japan Steel-Piping Co., who authorized the publication of this research, and to those others in various capacities connected with him.

References

1. "Report on the Elevated Temperature Properties of Stainless Steels". ASTM Data Series Publication DS-S1, 1964.
2. Mimino, Nagao. Iron and Steel, Vol. 52, No. 4, 1966, p. 710.
3. Lewis, M. H. and B. Hattersley. Acta. Met., Vol. 13, No. 7, 1965, p. 1159.
4. F. B. Beckitt and B. R. Clark. Acta. Met., Vol. 15, No. 1, 1967, p. 113.
5. For example: Miyoshi, Yukotochi. Iron and Steel, Vol. 53, No. 4, 1967, p. 570. —, Sumitomi Metals, Vol. 19, No. 4, 1967, p. 503.
6. Imai: Iron and Steel, Vol. 51, No. 13, 1965, p. 2336.
7. Nakagawa, Otsuguro. Tsuchiya: Iron and Steel, Vol. 45, No. 11, 1959, p. 1276.
8. Nakagawa, Otsuguro. Metal Materials Technical Research Report, Vol. 4, No. 1, 1961, p. 1.
9. For example: Okamoto, Tanaka and Fujimoto. Iron and Steel, Vol. 49, 1963, p. 613.

10. Nakagawa, Otsuguro. Iron and Steel, Vol. 46, No. 5, 1960,
p. 566.
11. Kinoshita. Iron and Steel, Vol. 53, No. 11, 1967, p. 1248.
12. Murray, J. D., J. Hacon and P.H. Wannell: I.S.I. Publication,
Vol. 97, 1966, p. 403.
13. Hopkin, L. M. and L. H. Taylor. J. Iron Steel Inst., Vol. 205,
No. 1, 1967, p. 17.
14. Kawabe, Nakagawa. Iron and Steel, Vol. 53, No. 1, 1967, p. 46.
15. Kawabe, Nakagawa and Mukaiyama. Iron and Steel, Vol. 54, No.
1, 1968, p. 48.
16. Tanaka, Suzuki. Iron and Steel, Vol. 54, No. 4, 1968, p. 229.
17. Tanaka, Shinoda. Iron and Steel, Vol. 51, No. 11, 1965, p.
2123.
18. Kawabe, Nakagawa and Mukaiyama. Iron and Steel. Vol. 54, No.
4, 1968, p. 218.
19. Tanaka, Shinoda. Unpublished.
20. Mimino, Kinoshita and Minegishi Shinoda. Iron and Steel,
Vol 54, No. 4, 1968, p. 464.
21. Miyoshi, Kazui. Metals Institute Journal, Vol. 25, No. 9,
1961, p. 581.
22. Orida, Yoshii and Uehara Katayama. Metals Institute Journal,
Vol. 25, No. 4, 1961, p. 241.
23. Orida, Katayama and Koyama Uehara. Metals Institute Journal,
Vol. 26, No. 10, 1962, p. 664.
24. Miyoshi. Metals Institute Journal, Vol. 26, No. 8, 1962,
p. 513.
25. Shinoda, Mimino and Minegishi Kinoshita. Iron and Steel,
accepted for publication.
26. Orida, Katayama and Koyama Uehara. Metals Institute Journal,
Vol. 26, No. 10, 1962, p. 669.
27. Yukitoshi. Iron and Steel, Vol. 54, No. 5, 1968, p. 584.
28. Tanaka. Gakushin 123 Committee Report, Vol. 8, No. 2, 1967,
p. 185.

/1486

29. McLean, D. Mechanical Properties of Metals: Willy, 1962.
(Tanaka, Kometani, Nunomura trans.: Mechanical Properties
of Metals. Kyōritsu Shuppan, 1966, p. 329).
30. Grant, N. J. The Strengthening of Metals. Reinhold, 1964,
p. 163.
31. Ansell, G. S. and J. Weertman: Trans. AIME, Vol. 215, 1959,
p. 838.
32. Unckel, H. Metall, Vol. 21, No. 5, 1967, p. 419.

Discussion

[Question] Metal Materials Technical Research Center; Yoshikuni
Kawabe

Is there any special significance to the fact that Ti and Nb
were added in a compound? That is, do you think that with the com-
pound addition of Ti and Nb, there is an interaction? If that is
your assumption, what do you think is the cause?

[Answer]

If you compare the cases where Ti or Nb is added separately
and where Ti and Nb are added together, the increase in creep rupture
strength is far more marked in the compound addition than in the
single — and particularly, when the atomic ratio of C/(Ti + Nb) has
a value of 4, the creep rupture strength is greatest. For example,
when C is 0.15%, an adequately high strength is obtainable with a
combined quantity of Ti and Nb under 0.3%. However, when we compare
the creep rupture strength [Figure 4 (a)] at 700° C of NB 34 steel
— to take an example of single addition of Nb — which has C 0.14%
and Nb 0.34%, and the creep rupture strength of TN5 steel (Figure 8),
a steel with Ti and Nb added, which includes about the same amount
of C, there is clearly a difference between them. TN5 steel shows a

high strength. From this result, too, we may believe that an interaction of Ti and Nb exists in Type 304 steel.

With regard to the reason for the interaction, the simultaneous addition of Ti and Nb causes a slowdown in the coalescence speed of the carbide $M_{23}C_6$, which precipitates during creep. As a consequence, the distribution pattern of the fine carbide improves, and contributes, we think, to the improvement in strength. But as to the strengthening mechanism, that is not clear and is currently under study.

Translated for National Aeronautics and Space Administration under contract No. NASW 2483, by SCITRAN, P. O. Box 5456, Santa Barbara, California, 93108